1968 CONFERENCE ON CITRUS CHEMISTRY AND UTILIZATION

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ABSTRACTS OF PAPERS

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OXIDATION OF ALCOHOLS, ALDEHYDES, AND PHENOLS BY ENZYME PREPARATIONS FROM CITRUS JUICE

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The primary alcohols in the homologous series from methanol to decanol, except heptanol, have been found in orange essence. None of them noticeably possesses the characteristic flavor and aroma of orange so that their major contribution to essence is probably in the fruit as precursors for aldehydes and other flavor compounds. To understand this precursor function of the alcohols with the view towards its control, the oxidation of alcohols and aldehydes by enzyme preparations from orange juice was examined. The role of phenol oxidation in maintaining the redox state of the coenzymes in these reactions was also examined.

Most of the known enzyme reactions involving the oxidation of primary alcohols are bimolecular with the coenzyme, nicotinamide-adenine dinucleotide (NAD). Therefore, the principle reaction studied has been:

$$\text{Alcohol} + \text{NAD} \xleftrightarrow[\text{dehydrogenose}]{\text{Alcohol}} \text{aldehyde} + \text{NADH}_2$$

The rate of reaction for each alcohol and aldehyde was measured by following the formation or disappearance of $NADH_2$ spectrophotometrically at 340 mμ. Solubility of the higher molecular weight compounds was aided by the addition of Tween 80.

The enzyme preparations were separated from neutralized orange juice by salt precipitation. In some cases they were purified further by dialysis and by differential adsorption on cellulose ion exchange columns.

Table I lists the oxidation rate for an orange juice enzyme preparation with ten alcohols relative to the rate with ethanol. Little or no oxidation was obtained with C-7 to C-10 alcohols.

This same enzyme preparation catalyzed the reverse reaction. The relative reduction rates shown in Table II indicate that acetaldehyde, butanal, hexanal, and octanal are the preferred substrates. These four aldehydes are present in orange essence; propanal, pentanal and heptanal have not been detected in essence. This reverse reaction with the aldehydes is faster than the forward reaction. The ratios of the absolute reduction-oxidation rates shown in Table II increase in the series from acetaldehyde to octanal.

This demonstration that orange-essence alcohols can be reversibly oxidized by enzyme preparations from the fruit suggests that similar reactions probably occur in vivo. Furthermore, if these are the major reactions for the alcohols and aldehydes in the fruit, then their steady-state concentration will be greatly influenced by these reactions.

The oxidation of aldehydes by orange juice-enzyme preparations does not follow the pattern described for alcohol oxidation. Glyceraldehyde-phosphate is oxidized by the enzyme preparation in a NAD-specific bimolecular reaction but acetaldehyde does not participate in this reaction.

Acetaldehyde reacts with the indicator 2,6-dichlorophenol in the presence of the enzyme preparation, however. This redox indicator gives a measure of the reaction rate. Hexanal, octanal and decanal do not replace acetaldehyde in this reaction.

The aldehydes and acids may be enzymically interrelated through some derivative. Very active phosphatase activity has been observed in orange juice preparations. This may have hydrolyzed phosphorylated derivatives to inactive free forms.

Also investigated was the role of phenols as intermediates in the reoxidation of $NADH_2$ to NAD. The ratio of $NADH_2$ to NAD affects the rates of alcohol oxidation and of aldehyde reduction by alcohol dehydrogenase. Therefore, in order to control reactions forming alcohols or aldehydes the redox ratio of NADH, to NAD must be controlled.

Table III lists the ortho- and para-diphenols that are oxidized by purified enzyme preparations from orange juice. Several of these diphenols and methoxy phenols are present in orange juice. The para-quinone, formed by the oxidation of p-quinol can function as the oxidant in the enzymic reoxidation of $NADH_2$ to NAD. The sequence of reactions for the oxidation of $NADH_2$ by O_2 through quinone is as follows:

$$\text{p-quinone} + NADH_2 \longrightarrow \text{p-quinol} + NAD \qquad (1)$$

$$\text{p-quinol} + 1/2\ O_2 \longrightarrow \text{p-quinone} + H_2O \qquad (2)$$

Total $$NADH_2 + 1/2\ O_2 \longrightarrow NAD + H_2O$$

Both reactions (1) and (2) have been demonstrated with enzyme preparations from orange vesicles.

Thus, orange juice contains enzymes that can effect the reversible oxidation of alcohols to aldehydes. The coenzymes reduced in these reactions can be reoxidized with O_2 through the intermediacy of p-quinones. These reactions may be significant in the synthesis of flavor compounds such as aldehydes from alcohols in the fruit. However, conventionally squeezed orange juice does not support these reactions. These enzymes would not be expected to affect flavor of processed and stored juice except through their influence on fruit from which the products are derived.

Table I

NAD - Specific Alcohol Dehydrogenase Activity

$$\text{Alcohol} + \text{NAD} \xrightarrow{\text{pH } 9.6} \text{aldehyde} + \text{NADH}_2$$

Alcohol	Relative Oxidation Rate
Methanol	0
Ethanol	1.0
Propanol	0.24
Butanol	0.22
Pentanol	0.20
Hexanol	0.18
Heptanol	0.03
Octanol	0.02
Nonanol	0
Decanol	0

Table II

NAD - Specific Aldehyde Reductase Activity

$$\text{Aldehyde} + NADH_2 \xrightarrow{pH\ 6.5} \text{alcohol} + NAD$$

Aldehyde	Relative Reduction Rate	Reduction Rate / Oxidation Rate
Acetaldehyde +	1.0	5
Propanal	0.15	3.6
Butanal	0.48	13
Pentanal	0.18	5.4
Hexanal	0.48	16.5
Heptanal	0.15	30
Octanal	0.32	89
Decanal	0.11	∞

Table III

Phenols Oxidized by Orange Enzyme Preparations

O-OR p-Diphenols	O-Methoxy-phenols
Catechol	Ferulic acid
Quinol	Feruloyl putrescine
Ubiquinol	Hesperetin
O-dihydroxyphenylalanine	Hesperidin
Chlorogenic acid	
Catechin	
Quercetin	
Quercetrin	
Rutin	
Eriodictyol	

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THE COMPOSITION OF THE "CARBONYL" FRACTION OF VALENCIA ORANGE PEEL OIL

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The isolation and identification of the flavor components contained in the volatile portion of orange peel oil has been a subject of considerable research by the Fruit and Vegetable Products Laboratory as well as others. Since most of the orange flavor can be found in this volatile fraction of the peel oil, research on the composition of this fraction is considered important as a basis for eventual formulation of orange flavor in terms of a group of compounds isolated from orange and possessing the basic orange flavor.

The "carbonyl" fraction represents the last remaining unidentified group of compounds in the volatile portion of Valencia orange oil, the hydrocarbon and alcohol fractions having been dealt with in earlier publications. The seventeen aldehydes and ketones and three esters contained in this fraction are listed in Table I.

Table I

"Carbonyl" Components of Valencia Orange Oil

1. n-hexanal
2. n-heptanal
3. n-octanal
4. 6-methyl-5-hepten-2-one
5. n-nonanal
6. trans-limonene oxide
7. cis-limonene oxide
8. octyl acetate*
9. citronellal
10. n-decanal
11. n-undecanal
12. neral*
13. geranial*
14. n-dodecanal
15. carvone
16. perillyl acetate*
17. perillyl aldehyde*
18. 1,8-p-menthadiene-9-yl acetate*
19. piperitenone
20. aldehyde A
21. nootkatone
22. β-sinensal
23. aldehyde B
24. α-sinensal
25. aldehyde C
26. aldehyde D
27. aldehyde E

*Isolated and identified as a component of Valencia orange peel oil for the first time.

The underlined compounds in Table I represent the most abundant constituents as estimated from the relative size of the peaks in the gas-liquid chromatogram. All of these abundant constituents have

potent and distinctive odors which probably contribute significantly to the characteristic orange aroma. The saturated aliphatic aldehydes contribute a sweet pungent fatty odor: neral, geranial and citronellal a pungent citrus-like odor, carvone a minty odor, nootkatone the odor of grapefruit and the sinensals a sweet pungent penetrating smell.

Trans- and cis-limonene oxide have never been reported as constituents of cold-pressed orange oil although not carbonyl containing compounds, they were included because they are found in one of the fractions along with the carbonyl compounds. A number of the alcohols in orange oil are related to limonene oxide and are possibly formed by acid-catalyzed ring opening of the oxides.

Aldehydes A-E represent a series of α,β-unsaturated aldehydes with the general formula $R\text{-}CH{=}\underset{\displaystyle R'}{\underset{|}{C}}\text{-}CHO$ where R and R' are saturated straight-chain hydrocarbon radicals, $CH_3(CH_2)_n$- with n=5,6,7, or 8. These aldehydes are formally related to the straight chain saturated aldehydes present in relatively large quantities in orange oil, octanal, nonanal, and decanal, by acid-catalyzed aldol condensation according to the following set of equilibria:

$$R\text{-}CHO + R'CH_2CHO \overset{H^+}{\rightleftharpoons} \underset{\displaystyle OH\ \ R'}{R\text{-}\underset{|}{CH}\text{-}\underset{|}{CH}\text{-}CHO} \overset{H^+}{\underset{H_2O}{\rightleftharpoons}}$$

$$R\text{-}CH = \underset{\displaystyle R'}{\underset{|}{C}}\text{-}CHO + H_2O$$

Whether or not such an equilibrium exists and the extent to which it influences the flavor of natural orange products has not been established. The α,β-unsaturated aldehydes themselves contribute little to the flavor other than a faint, burnt fatty quality.

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THE CHEMISTRY OF DELAYED BITTERNESS IN CITRUS JUICES

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Certain citrus juices (early- to mid-season Washington Navel, Shamouti, and Australian Valencia oranges) gradually become bitter on standing or during processing, whereas, the fruit when eaten fresh or the juice immediately after preparation are not bitter. This phenomenon, which was noted many years ago, is generally referred to as delayed bitterness.[1] The bitter principle of processed navel orange juice is the triterpenoid dilactone called limonin (Figure 1). The presence of limonin in bitter navel orange juice was reported (Higby, 1938) even before the complete structure of the compound was known (Arigoni, et al., 1960). Subsequent work has confirmed that limonin is the only limonoid present in bitter navel orange juice (Emerson, 1949; Maier and Beverly, 1968), and that limonin also is found in grapefruit juice (Maier and Dreyer, 1965), under certain conditions in Valencia orange juice (Kefford, et al., 1952), and Shamouti orange juice (Samisch and Ganz, 1950). However, the reason for the delayed development of bitterness in citrus juices has remained unresolved over the years.

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1 The delayed bitterness of orange juice should not be confused with the bitterness of grapefruit and the Seville orange. Both of these fruits are bitter when eaten fresh as well as when made into juice. The compounds responsible for the bitterness of fresh grapefruit and Seville orange are flavanone neohesperidosides (Horowitz, 1961).

Recent research carried out in our laboratory has led to an explanation of the delayed bitterness phenomenon (Maier, 1968). This paper presents a summary of the results of that research. The individual publications which contain the original reports of various phases of this work are cited throughout this paper and may be consulted for experimental details and further discussion.

Our research has shown that, whereas, the bitter compound limonin occurs in navel orange juice after the juice becomes bitter, it does not occur in the tissues of the healthy, intact fresh fruit to any significant extent. Rather, a close relative of limonin which is a nonbitter compound; namely, limonoate A-ring lactone (Figure 2) (a new compound) is found (Maier and Margileth, 1967; Maier and Beverly, 1968). This compound differs from limonin in that in aqueous solutions it is nonbitter at 50 p.p.m., whereas, limonin is detectably bitter at 2-7 p.p.m. and extremely bitter at 15-20 p.p.m. Limonoate A-ring lactone was found to occur in the structural tissues of the endocarp and in the albedo of the peel of navel oranges and grapefruit. In addition, the limonoate A-ring lactone was found to be readily converted into limonin in solutions having the same acidity as orange juice. Therefore, in juice manufacture when the broken tissues of the fruit mix with the acidic juice, the nonbitter limonoate A-ring lactone, which is unstable under these conditions, is converted into the bitter compound limonin and the juice gradually becomes bitter. If the juice is heated, the rate of conversion of the nonbitter compound into limonin is increased and the juice becomes bitter more rapidly.

Higby (1941) reported that bitterness of navel orange juice could be minimized by avoiding tissue maceration and by immediately separating the coarser tissue fraction from the extracted juice. The chemical basis of this process is now clear. Avoiding maceration retards extraction of limonoate A-ring lactone into the liquid phase and at the same time facilitates removal of this potential source of bitterness before limonin is formed. It is hoped that these new findings will both aid and stimulate the commercial application of this process.

During work on the identification of the limonoate A-ring lactone (Maier and Margileth [In Press]), we discovered an enzyme in fruit tissue extracts which catalyzes the conversion of limonoate A-ring lactone to limonin in acidic solutions. This enzyme appears to be responsible for the traces of limonin occasionally encountered when extracting limonoate A-ring lactone from the fruit tissues. It may be partly responsible for the conversion of limonoate A-ring lactone into limonin in orange and grapefruit juices during commercial juice preparation. We have subsequently isolated and purified the enzyme and studied its properties (Maier, Hasegawa, and Hera [In Review]).

Another well known but unexplained aspect of the delayed bitterness phenomenon is the fact that at varying times after commercial maturity is reached (depending on the year) navel oranges will produce juice that

does not become bitter after standing or processing. In a study of navel oranges at different stages of maturity (Maier and Beverly, 1968), we found that limonoate A-ring lactone gradually disappears from the tissues as the fruit ripens beyond commercial maturity and that the limonin content of the juice made from these fruit follows a parallel course. Thus, the juice made from navel oranges whose tissues contain no limonoate A-ring lactone contains no limonin and is nonbitter.

On the basis of these studies, it can be concluded that limonin does not occur to any significant extent in the tissues of intact, healthy oranges or grapefruit, although it is a natural constituent of citrus seeds. Rather limonoate A-ring lactone, a nonbitter compound, is present in these tissues. On the other hand, limonin may be found as a constituent of intact fruits in instances where the fruit has been damaged and the acids and enzymes released from the damaged tissues have brought about conversion of the limonoate A-ring lactone into limonin. This is probably the reason for the bitterness occasionally observed where oranges have been damaged by frost before reaching commercial maturity.

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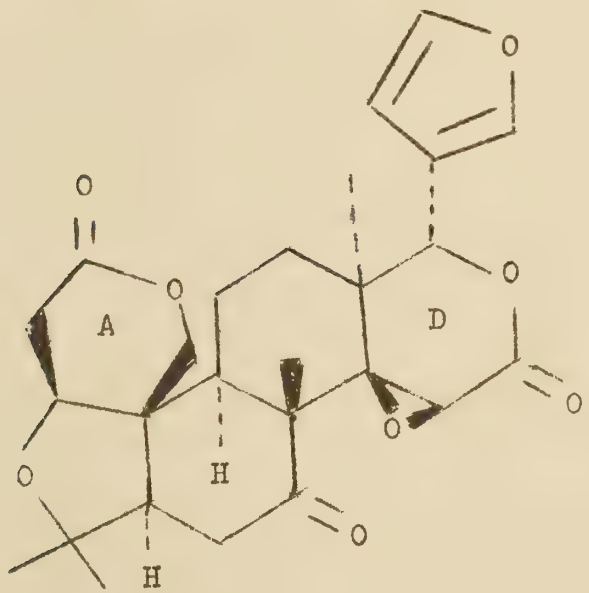

Figure 1.--Structure of limonin (bitter).

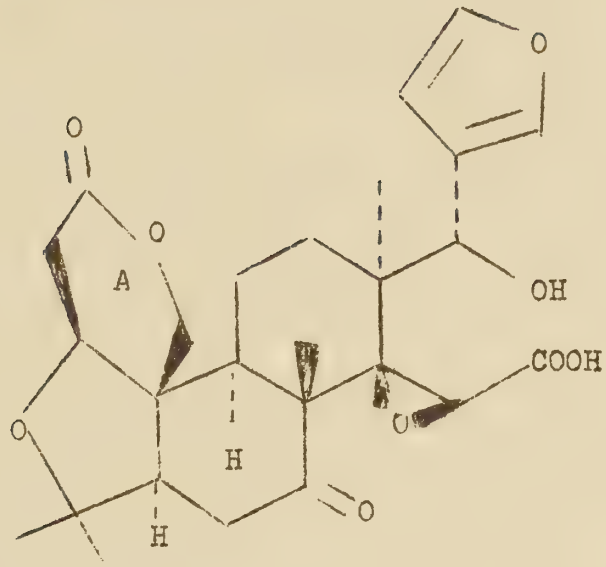

Figure 2.--Structure of limonoate A-ring lactone (nonbitter) shown as the free acid.

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DIFFERENTIAL FATTY ACIDS STUDIES OF SEEDS AND JUICE FROM SEVERAL CITRUS SPECIES

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Lipid oxidation has been implicated as one of the causative factors in flavor deterioration of processed juice. Available information in other food product areas indicates that oxidation of unsaturated fatty acids, especially the highly unsaturated acids, is a contributing factor to off-flavor development. To further understand the role of lipids in flavor deterioration, we have undertaken a preliminary study of the fatty acid composition in seeds and juice from several citrus species.

Juice and seed fatty acid methyl esters were identified by employing several criteria, viz. (a) comparison of retention time to those for standards, (b) separation of fatty acids on silver nitrate impregnated thin-layer plates according to the degree of unsaturation, (c) hydrogenation of methyl esters to yield saturated carbon skeltons, and (d) plots of log retention time versus carbon number from data derived from nonpolar (OV101) and polar (DEGS) columns to yield information on effective chain lengths.

Fatty acids were analyzed in juices from Persian lime, Valencia orange, Marsh grapefruit, Eureka lemon and tangerine. Seed fatty acids were examined in Valencia orange, Marsh and Duncan grapefruit, Eureka lemon and tangerine. The major fatty acids detected in juice and seeds

are shown in Tables I and II, respectively. These acids taken collectively comprise greater than 95% of all acids in juice and greater than 99% in seeds.

The vast majority of seed acids belong to the even carbon series with chain lengths of sixteen and eighteen carbon atoms predominating. Acids with even carbon lengths below sixteen and above eighteen are found in trace amounts. Heptadecanoic acid was the only odd carbon acid to be detected in trace amounts. The fatty acid composition of juice is extremely complex and manifests numerous trace acids. While the even carbon series dominates, odd carbon acids from C_{15}-C_{25} have been detected in trace amounts. The presence of branched-chain acids has also been detected in trace quantities.

TABLE I

MAJOR FATTY ACIDS OF CITRUS JUICES (MOLE %)

	FRUIT				
Fatty Acid*	Orange	Grapefruit	Lemon	Lime	Tangerine
16:0	19.4	21.5	22.9	20.8	19.6
16:1	4.6	3.9	1.0	4.0	4.5
18:0	0.7	1.2	3.1	2.2	1.0
18:1	25.7	21.0	7.0	15.6	33.3
18:2	31.6	36.2	41.2	32.9	25.4
18:3	7.8	10.7	17.0	17.3	11.9
22:0	0.3	0.2	0.6	0.4	0.3
24:0	0.7	0.7	1.4	1.3	0.6
26:0	0.5	0.4	0.7	0.8	T

* No. of Carbon Atoms: No. of Double Bonds

T = trace, $< 0.1\%$

TABLE II

MAJOR FATTY ACIDS OF CITRUS SEEDS (MOLE %)

	FRUIT				
Fatty Acid	Orange	Duncan Grapefruit	Marsh Grapefruit	Lemon	Tangerine
16:0	27.8	28.8	29.5	20.4	22.5
16:1	0.9	0.7	0.5	0.5	0.5
18:0	4.9	3.0	2.5	3.1	4.5
18:1	26.0	20.9	20.1	26.3	22.7
18:2	37.1	42.2	41.7	38.0	45.3
18:3	3.2	4.0	4.9	11.1	4.0

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SYNTHETIC SWEETENERS FROM CITRUS BYPRODUCTS

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The consumption of noncaloric sweeteners has increased rapidly in the past 5 or 6 years. This expansion is likely to continue. The most important factor supporting this conclusion is the expected growth in sales of soft drinks, and the proportion of these products which is likely to be made with noncaloric sweeteners.

At the present time, cyclamate and saccharin are the only two important noncaloric sweeteners in use throughout the world. In 1965, the U. S. production of cyclamate was 10.3 million pounds, and saccharin was 2.6 million pounds. Together they had a value of $11.7 million. It is estimated that by 1970, U. S. consumption will be about 21 million pounds of cyclamate and 4 million pounds of saccharin.

The dihydrochalcones are characterized by their pleasant sweetness and no bitter aftertaste. The onset of sweetness is relatively slow but it is long lasting. By combining these substances with cyclamate, it appears that a taste profile, very much like that of sucrose, can be obtained. The long lasting sweetness of the dihydrochalcones might make them useful also in a number of products in which noncaloric sweeteners have not been used in the past; such as, chewing gums, medicated troches, or mouth washes.

If one-half (in terms of sweetening power) of cyclamate and of saccharin were to be replaced by naringin dihydrochalcone or hesperidin glucoside dihydrochalcone, it would represent an annual market for about 6.1 million pounds by 1970. Currently hesperidin and

naringin sell for around $8 per pound, but if a large demand for them were to develop, the price might well drop to $1 per pound. Since about 1.5 pounds of the citrus flavanones would be required to make 1 pound of dihydrochalcones, this would represent sales of about $9 million per year for the citrus industry by 1970. In addition, chemical manufacturers who convert the flavanones to dihydrochalcones would have sales of $11 million worth of the finished product.

Some of the procedures and problems of converting the starting materials to the final products will be discussed.

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STUDIES ON HYDROXYMETHYLFURFURAL RELATIONSHIP TO HEAT TREATMENT AND STORAGE IN ORANGE JUICE PRODUCTS

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Quality of some processed foods has been related to their hydroxymethylfurfural (HMF) content, because HMF formation parallels off-flavor development in these foods. HMF concentration is an index of the amount of nonenzymic browning undergone by these foods during heat or storage treatment. In honey, for example, determining the HMF content involves dilution with water, treatment with p-toluidine and barbituric acid, and quantitative measurement of absorption at 550 mm of the pink-colored derivative formed. Even fresh honey collected under the most carefully controlled conditions contains measureable amounts of HMF. In both apple and grape juices, quality can be correlated with HMF content by this method.

Foam-mat dried instant orange juice (IOJ) undergoes a flavor change after storage that has been qualitatively correlated with HMF formation. The results reported below concern our efforts to make a quantitative correlation between HMF content and off-flavor development in IOJ.

The color test that is successful on honey and on single-strength apple and grape juices was not sensitive enough to detect HMF in single strength reconstituted IOJ. Thus, a procedure was developed to concentrate the total HMF from 168 g. of IOJ powder into a small volume suitable for spectrophotometric measurement. The concentration procedure involves:

GENERAL PROCEDURE

a. Making a slurry of 168 g. IOJ and 300 ml. of 1:1 acetone-water.

b. Extracting the slurry with several 300 ml. portion of ether.

c. Concentrating the combined ether extract to small volume under vacuum, adding 10 ml. H_2O, and removing the rest of the ether.

d. Filtering the aqueous residue through glass wool.

e. Adjusting the filtrate volume to exactly 10 ml.

f. Preparing a blank from 5 ml. of this filtrate, 12.5 ml. of p-toluidine solution and 2.5 ml. of water.

g. Preparing the colored derivative by treating the other 5 ml. of filtrate with 12.5 ml. of p-toluidine and 2.5 ml. of barbituric acid solution.

h. After 3-5 min., measuring the visible absorption of the colored derivative above versus the blank at 550 nm with a Cary 14 spectrophotometer.

i. Comparing the absorbance with a standard curve prepared from known concentrations of HMF derivative to determine the HMF content.

Reagents: p-Toluidine solution was prepared by dissolving 25 g. of p-toluidine in 125 ml. of isopropanol and 25 ml. of acetic acid, then diluting to 250 ml. with isopropanol. Barbituric acid solution was prepared by dissolving 500 mg. of barbituric acid in 100 ml. of water.

Previous reports noted that maximum color development in this reaction was not reached for 3 to 4 minutes. No mention was made of

subsequent color loss with time. Our results showed that considerable decrease in absorbance occurred with time. Thus, measurements should be made in 3-5 minutes after mixing reagents.

A standard curve was prepared using a series of known concentrations of HMF and the results are given in Table 1. Values for absorbance obtained from IOJ samples were compared with a curve prepared from these standard values to obtain the quantity of HMF present.

Samples of IOJ that had been stored at 85°F for seven weeks, three days were analyzed using the procedure described above. The number of ether extractions was varied holding the rest of the procedure constant to determine the smallest number of extractions permitted without appreciable loss of absorbance. The results of this study are presented in Table 2. Four extractions with ether seem to be sufficient. Control IOJ that had been at -5°F for the same length of time as the samples in Table 2 had no appreciable absorbance.

Table 1

Standard HMF Tabulation for Known Samples

(Five Minutes Color Development)

HMF Concentration (mg/ml)	Absorbance
0.0125	0.23
0.025	0.44
0.0375	0.60
0.050	1.00
0.075	1.43

Table 2

Extraction Efficiency for HMF Determination in Stored IOJ

(Five Minutes Color Development)

Number of Ether Extractions	Absorbance	Amount of HMF mg.
6	0.54	0.33
5	0.46	0.28
4	1.02	0.54
3	0.33	0.19

Conclusions from these results on off-flavor instant orange juice are:

a. Measurable amounts of HMF are formed in stored IOJ when off-flavors have developed.

b. Concentration of the HMF present is required to obtain meaningful results.

c. Preliminary results indicate that correlation of HMF content with off-flavor development is possible.

The applicability of this test for correlating HMF content to degree of heat treatment in canned and chilled single strength orange juice (SSOJ) is being studied. With commercial samples of canned SSOJ there was not enough HMF present to detect in SSOJ without prior concentration. In this case, ether extraction of SSOJ afforded sufficient concentration of the HMF to give measurable quantities. The concentration procedure was as follows:

a. Extracting 46 oz. of juice in a separatory funnel with 4 x 250 ml of ether.

b. Concentrating the combined ether extract to small volume as was done in step C of the General Procedure for IOJ and repeating the remainder of the procedure.

Absorbance values averaged 0.9, and quantities of HMF averaged 0.50 mg. per 46 oz. can of juice. A noteworthy observation here was that the typical odor of canned SSOJ was concentrated in water-insoluble solids trapped by the glass wool plug in step d of the General Procedure. This typical canned juice odor is quite different from the off-flavor of IOJ.

Table 3

HMF Content of Stored Chilled Juice Samples

	Absorbance		
Time (Weeks)	Cold pack glass	Hot pack glass	Hot pack canned
0 (control)	0.02	0.02	0.03
2	0.07	0.00	0.04
6	0.07		
7		0.12	
9	0.08	0.08	

Chilled juice packed under three different sets of conditions was prepared by Dr. Wenzel at the Citrus Experiment Station at Lake Alfred and stored at 85°F for up to nine weeks. Results of those tests to date are given in Table 3.

Conclusions from these studies on canned and chilled SSOJ are:

a. Off-flavor components different from those responsible for off-flavor in IOJ are probably being formed rapidly here.

b. Concentration of these off-flavor components in an ether-soluble, water-insoluble fraction was observed.

c. Studies on the composition of this off-flavor fraction may lead to a test for storage changes in SSOJ.

d. Quantitative HMF test appears of little help in following storage changes in SSOJ because of the small amount formed.

sol

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ORANGE JUICE TABLETS - A NEW CITRUS PRODUCT

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Previous studies have shown that foam-mat dried citrus juices require densification for improved reconstitution properties. Undensified, ground foam-mat powder was extremely light and fluffy and tended to float and clump when reconstituted. Methods were developed for increasing the bulk density of this powder by passing it through the nip of hard, heavy, steel rolls where pressure was applied forming small, flat, dense flakes. These flakes were then ground to give a powdered material of a much increased bulk density. Studies were undertaken to determine the relationship between densification, changes in bulk density, and the fragility of the densified powder particles.

In order to study these matters, an experiment was undertaken to form small, flat discs at different pressures, and to determine the amount of shear required to break these discs as an index of fragility. During this experimentation, samples were prepared which varied in moisture content from 0.9 to 1.6% and these were subjected to pressures of 3,800 to 19,100 psi by a ram driven hydraulic press (Carver press). This formed small, firm citrus discs which were then tested in a shear press to determine the amount of shear required to break them. While this experimentation was being carried out, a number of experimentors began eating these discs from time to time and found they were very tasty.

This suggested the possibilities of compressing citrus solids into a form for consuming like candy, as opposed to the more traditional idea of dissolving dehydrated citrus solids to reconstitute to juice.

Following this idea which could lead to development of a new product, experiments were planned for producing various types of fruit juice solids in tabletted form for eating. A pilot model tabletting machine was installed with the capability of producing as many as 90 tablets per minute. Punches and dies used with this machine initially were 1/2-inch in diameter. Tablets produced to this time have been about .8 gms. in weight, 1/2-inch diameter flat-faced discs, and 3/16-inch thick. Subsequent studies have shown that approximately 3,000 psi is required on the tablet punch to form these tablets.

Experiments were also conducted to determine what type of tabletting, binding and releasing agent would be required to make smooth, clean, dust-free tablets which would release easily from the machine. A commercial stearate triglyceride was found effective for this purpose. This is a granular form of a completely edible food product similar to commercial hydrogenated vegetable oils used as shortenings. There are no limits on the safe use of this material in foods. It has been found effective as a tablet binder and release agent in amounts from 1/2 to 2% (solids basis). The percent of binder was varied and it was found effective with citrus solids at about 0.25% when densified powder was used and about 0.5% when undensified powder was used.

These tablets have been prepared from orange-plain, sweetened with sugar and sweetened with cyclamate; grapefruit-plain, sweetened with sugar and sweetened with cyclamate; and a combination referred to as

"Citrus Punch" - grapefruit, lime and strawberry, sweetened with sugar. The process would appear to be applicable to most any other kind of high sugar-containing solids.

A brief study has been made of the manufacturing costs, involved in producing these tablets. Basically, if orange solids are about 55 cents per pound, (closing prices last season), and foam-mat drying costs run about 8 cents per pound solids, and assuming the loss and additional costs for compressing these solids into tablets is practically negligible, then a pound of citrus solids can be converted to tablets for approximately 65 to 70 cents. This pound of powder will make a substantial number of tablets, the exact number being dependent, of course, upon the size chosen for the tablets. Using tablets of the current size (1/2-diameter) which are equivalent to about 1/4 ounce of orange juice each, over 500 tablets can be prepared from one pound of dehydrated juice powder. Of course, even more can be made from this amount of citrus solids when sugar is added. Packaging will add substantially to the cost of production but should not be prohibitive.

Several different types of packaging have been used. They have included foil/poly/paper sealed envelopes, foil/poly envelopes, screw-cap glass jars, and plastic push-cap glass vials. All of these packages have been found suitable. A plain poly pouch was not found suitable. There is some question as to whether cellophane envelopes such as used for candies of this type might be suitable. They have not been tested to date, but the principal protection required is a moisture barrier.

Studies are presently underway to determine the relative nutritive aspects of these tablets as compared to the original powder, and the original juice from which they were made. Preliminary studies have shown that the ascorbic acid content of these tablets runs about the average value for orange juice.

Considerable interest has been shown in these tablets by pharmaceutical companies as well as different food and candy companies. Most interest is directed toward their potential as camping foods, nutrition supplements, diet foods, and the like. They also offer considerable interest by virtue of affording a means for citrus to compete in a field which has heretofore been exclusively the field of synthetic materials.

Attempts have been made to eliminate the natural hygroscopicity of these tablets by coating them. They have been dipped in aqueous solution of methylcellulose and carboxymethylcellulose polymers of different types. They have also been tested with an alcoholic solution of cellulose polymers. Other possibilities which have been tried included dusting with silica or starch. None of these coating methods has met more than a moderate degree of success to date.

A number of materials are being studied as flavor enhancement additives. These include commercial "locked-in" cold-pressed peel oil and several different types of "essence" extracts adsorbed onto dry hydrophilic silica as carrier. These studies are still in progress.

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UTILIZATION OF WHOLE GRAPEFRUIT AND ORANGES - A PROGRESS REPORT

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(To be presented by F. P. Griffiths)

Whole oranges or grapefruit were cooked 5 minutes at 15 p.s.i.g., in a modification of the process of (Braverman and Levi, 1960). The cooked fruit were comminuted in Chisholm-Ryder screw finisher, using a screen with 0.062-inch openings. The harder portions of the fruit, including scaly portions of the peel, most of the rag, and the seeds, were separated and rejected in this operation; the seeds remained whole. Rejected material from a 90-pound box of oranges was 8-3/16 pounds. The softer portions of the pulped fruit, amounting to approximately 90% of the total weight of the starting material, were homogenized in a Manton-Gaulin homogenizer. The homogenized material was canned and stored at -10° F. until utilized. Grapefruit puree was generally debittered with 0.2% naringinase (Kumitanase) for 2 hours at 45 to 50° C. prior to final utilization. Part of the puree was diluted 50% with water (2 l. water to 4 l. pulp) and the diluted pulp circulated through a Mojonnier low temperature evaporator at 150° F. until the pulp had regained its original volume. A reduction of 30 to 35% of the peel oil remaining in the fruit after the cooking operation was achieved.

The homogenized and homogenized-deoiled frozen purees were utilized in the preparation of citrus beverages and nectars of highly acceptable quality. A typical formulation consisted of 100 gm pulp, 125 gm sugar,

25 gm 6-fold lemon concentrate and water to 1 l. An orange beverage prepared from this formulation, packed in No. 2 plain cans and No. 303 enameled cans and stored at 70° F., has shown no significant deterioration after 150 days, as indicated by taste evaluation ratings.

The pulps have been utilized in citrus-flavored syrups and several other products. Consideration has been given to utilization of the purees in citrus-flavored baked goods.

Another approach to the improved utilization of citrus fruit involves the upgrading of various portions of the fruit now used only for cattle feed. Excess pulp removed from the juice in a finisher subsequent to fruit extraction was utilized along with the puree to obtain a beverage having body similar to hand-extracted juice from whole fresh fruit.

Acceptable syrups have been prepared by ion exchange treatment of citrus peel liquor pressed from the wet peel. Syrups having the best flavors were obtained by passing the liquor through an intermediate strength acid resin (cation form) and followed by treatment in a column of intermediate strength base resin (anion form). The use of lime ($Ca(OH)_2$) in the initial processing of the peel was found to cause, or accentuate, off flavor in the final syrup. By treating the ground peel with 0.3% Pectinol at 50° C. for 2 hours, to obtain juice release, instead of lime, this off flavor was avoided. The basic ion exchange resin reduced the naringin content of grapefruit peel liquor ten fold (0.044 to 0.004% naringin; 0.031 to 0.0036% by Davis test). From liquors obtained in the first pressings of peel (12 to 15° Brix), syrups of > 60° Brix were obtained by a 10:1 volume concentration (including ion

exchange treatment). The extracts obtained by resuspending the expressed peel in water, and pressing a second time (3 to 7° Brix) required about a 40-fold concentration to reach >60° Brix. Syrups prepared using the acid column first, followed by the base column, were blander than those prepared via the reverse procedure.

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STUDIES ON RECOVERY OF WATER SOLUBLE ESSENCES AND DISTILLED OIL FROM ORANGE PEEL

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Studies on the addition of essence to instant orange juice have indicated that more essence could be used than was available from the equivalent amount of fresh juice. The dried product is thoroughly stripped of volatile compounds during concentration and dehydration. A degree of "over-flavoring" is needed to compensate for the complete loss of volatiles. Also, it was obvious that an abundance of good flavor would mask slight processing flavor acquired during concentration and drying. In order to have an abundance of flavor to work with, sources other than fresh juice were considered.

A simple atmospheric unit has been devised for the recovery of volatile water soluble essences and distilled orange oil from peel slurries, extracts, juices and juice components. The apparatus consisted of a turbulent-film evaporator, a stripping column, a reflux column and condenser, and a chilled product condenser and receiver. The turbulent-film evaporator permitted the use of slurries and suspensions as well as ordinary citrus juices. The distilled oil and water-soluble essences collected in the receiver and formed two layers in an oil trap. The oil layer was decanted off, leaving the aqueous layer containing the water-soluble fractions of volatile flavor and aroma components.

In a few original experiments, various products were stripped on the turbulent film evaporator and the volatile distillate was simply condensed. This material was analyzed by GLC using methylene chloride extraction to remove and concentrate the organic materials. GLC analysis of these components stripped from a slurry of ground whole orange peel at atmospheric pressure was compared to a similar analysis of a commercial juice essence. This analysis showed the same general components were present in approximately the same relative concentrations in both samples.

On a pilot scale using essence recovery equipment capable of handling from 10 to 50 gallons of feed material per hour a number of different sources of experimental essence were studied. In most cases, the source material was ground, slurried with one or two parts of water, passed through a finisher, and the aqueous extract was used as a source for the "experimental essence." Among the sources compared were: orange albedo, orange flavedo, ground whole orange peel, whole peeled fruit, ground whole fruit, single strength orange juice, and peel oil desludger effluent. Essences obtained from these sources were compared on a basis of chemical oxidation demand (COD), ethanol content, and total organic extractables (TOE) less ethanol. On these basis all of these materials served as good prospective sources of experimental essence. They were evaluated for flavor potency or "fold" by a 12 man taste panel. Essences of highest flavoring power were obtained from orange flavedo and from ground whole peel. Essences from ground whole peel, peeled fruit, and single strength juice all were considered to improve the quality of juice products to which they were added.

GLC analyses were carried out on essences from these sources as compared with commercial juice essence. Most of the peaks seen in commercial essence were found also in essences from ground whole peel, ground flavedo, and ground albedo. The highest amount and greatest number of components were found in flavedo. In albedo a few of the more volatile components were reduced in amount. GLC analysis of the experimental essence from single strength orange juice was, for all practical purposes, identical to that from commercial orange essence. The experimental essence obtained from peel oil desludger effluents was similar in most respects to that of commercial orange essence except that a number of the highly volatile components were missing or greatly reduced.

Using commercial peel oil desludger effluent several experiments were carried out varying reflux ratio. The material was fed at 10 gal/hr into the turbulent film evaporator where approximately 25% was vaporized and passed into the stripping column. By controlling the temperature on the reflux condenser above the stripping column, the amount of aqueous vapors passing out the top of the stripping condenser (along with the distilled oil) was varied. The reflux ratios ranged from 2/1 to 20/1. The experimental essences were compared as before, on a basis of COD, ethanol, TOE, and TOE/°Brix of feed. They were also evaluated for "fold" and for quality as before. Generally, as the reflux ratio increased the TOE, and the TOE/°Brix feed increased. Highest fold achieved was about 1,000 in a sample which had been prepared at a reflux ratio of about 20. This sample also was judged very high in quality,

both in reconstituted concentrate, and foam-mat powder. COD varied from about 2 to about 15 ($\times 10^{-3}$), ethanol content varied from about 1 to about 7 ($\times 10^{-3}$), TOE ranged from about 0.1 to 1.4 ($\times 10^{-3}$), TOE/°Brix of feed ranged from about 0.078 to 1.162($\times 10^{-3}$). All values except ethanol tended to go up or down as a reflux ratio increased or decreased, respectively. However, ethanol content was quite variable with some slight trend toward a decrease of ethanol as reflux ratio increased.

Regular checks of column "bottoms" indicated absence of a significant amount of either oil or essence, indicating that all volatiles passed out the top of the reflux condenser and were condensed in the chilled water condenser. The concentration of TOE in the water layer was found to depend upon the ratio of water to distilled oil. The amount of oil remained constant. Within limits, the smaller the amount of aqueous phase the smaller the total extractables in the aqueous phase. When the volume of water was limited, more of the essences dissolved in the oil and it was apparently a question of partition.

In another series of experiments the percentage vaporization in the turbulent-film evaporator was varied from 8% to 27%. In each case the recovery of distilled oil was approximately 96% while the TOE varied only slightly. Ten percent vaporization seemed sufficient to recover most of the oil and other volatile organic material. Future experiments may reveal even smaller percentage vaporization to be adequate.

The total amount of flavoring material that can be obtained from a given amount of fruit is much larger from the peel than from the juice, but the concentration of the essence from the peel is lower

because of the larger amount of oil and the partition coefficient relationship. The layer of oil can be separated and the concentration of essence continued in a rectifying column.

At present the standards of identity for frozen concentrated orange juice provides for flavor fortification with orange peel oil and essence from juice and does not include essence from peel. Peel essence has good flavoring possibilities for many purposes, however.

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LIST OF CITRUS PUBLICATIONS

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Reprints of publications may be obtained without cost by addressing request to the Laboratory listed.

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